

A Study of One-Bath Alkali–Amine Hydrolysis and Silk-Fibroin Finishing of Polyester Microfiber Crepe Fabric

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ABSTRACT: In this study, the synergistic aminolysis (sodium hydroxide and ethylene diamine in one bath) mechanism of polyethylene terephthalate (PET) microfiber crepe fabric was preliminarily investigated. The results showed that not only active groups (i.e., —NHR, —COOH, and —OH) but also considerable cracks and craters were introduced onto PET fibers, which provided locations for a subsequent crosslinking reaction and mechanical attachment and so facilitated the silk-fibroin finishing. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1467–1473, 2001

Key words: aminolysis; alkaline hydrolysis; silk-like finishing; PET fiber; silk-fibroin finishing

INTRODUCTION

Silk fiber, “the queen of fibers,” is famous for its luxurious appearance, soft touch, scrooping feel, and healthy function to the human body. However, because of silk's small output, various silk-like fabrics¹ are needed to meet consumer requirements.

Japan takes a leading role in silk-like finishing, which has undergone five generational developments.² Of all the fibers, polyethylene terephthalate (PET) is the most promising silk-like-finishing mother fiber. Although silk-like techniques have been developed rapidly (e.g., alkaline hydrolysis, plasma treatment, chemical modification, and microfiber technology), the intrinsic shortcoming of PET has not yet been overcome; that is,

it has a very low moisture regain and thus results in inferior physiological and psychological wearing comfort compared with real silk.

Recently, a new and outstanding healthy finishing technique, silk-fibroin coating finishing,^{3,4} has been put forward by researchers to solve this problem. With the aid of a crosslinking agent, silk-fibroin molecules were fixed onto the PET fiber surface and small gaps between yarns to form a thin and soft silk-fibroin film, which was designed to improve the moisture absorbability and wearing comfort of the PET fabric.

However, because PET has a rigid, compact structure, a smooth surface, strong hydrophobicity, and almost no active groups, it is very hard for silk fibroin to locate on it, and only low silk-fibroin adduct and little absorbability improvement was gained. To change this passive and lazy role of PET in the silk-fibroin finishing, we used a new modification method, alkali–amine hydrolysis in one bath, in this study to introduce active groups for the silk-fibroin fixation on PET fiber.

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EXPERIMENTAL

Materials

PET Microfiber Crepe Fabric

Fabrics (warp yarn, 75 denier (d)/48 filament (f) heteroshrinkage composite yarn; weft yarn, 1 d/f) were supplied by Jianshu Textile Research Institute (Tianjin, China). The fabric was scoured and creped in one bath.

Reagents

Sodium hydroxide (NaOH), ethylene diamine, carbon tetrachloride, *n*-heptane, calcium chloride, 95% ethanol, glutaraldehyde, and so on were chemical reagents provided by Tianjin Chemical Reagent Co. (Tianjin, China).

A 10% water solution of Catalyst 1227 (Tianjin Institute of Textile Science and Technology, China) was used as a catalyst. The scouring agent was NICCA SUNMORL BK20F (Nicca Co., Ltd., Guangzhou, China). Acid Red G (BASF Co., Ltd., Shanghai, China) was also used.

Experimental Methods

1. The heat setting was 185°C × 30 s; the tension ruler was at 0.5 cm (Werner Mathis Stender AG LTF 97885, Zurich, Switzerland).
2. Alkaline (NaOH) hydrolysis or cohydrolysis with NaOH and ethylene diamine was performed in one bath (95°C × 90 min) with the catalyst. A soup washing (85°C × 15 min) and then warm water washing, dilute acetic acid washing, and cold water washing were performed until the fabric was in a neutral situation. Weight loss (WL) of the fabric was calculated as follows:

$$W \cdot L(\%) = [(W_0 - W_1)/W_0] \times 100$$

where W_0 and W_1 are fabric weights before and after hydrolysis, respectively.

3. The density of the weft yarn was tested by the density gradient tube method.⁵ The mixed solvent was made of tetrachloride carbon (CCl₄) and *n*-hexane, and the working range was 1.33729–1.4057 g/cm³ at 21 ± 0.2°C. If the density (d) for totally crystallized PET is 1.445 g/cm³ and the density for totally amorphous PET is 1.335 g/cm³, crystallinity, β , can be calculated with the following equation:

$$\beta/1.445 + (1 - \beta)/1.335$$

4. The modified fabric was dyed with 4% of the weight of the fabric of Acid Red G at a liquor

ratio of 1:100 at 95°C for 1 h, and then the loose color was washed off. The depth of the color was evaluated by the k/s value (where k is the absorbency factor of the colored substance and s is the scattering factor), which was tested with a Hitachi Type 330 spectrophotometer (Tokyo, Japan) ($\lambda = 515$ nm).

5. The modified fabric was immersed in a silk-fibroin solution at 95°C for 1 h and in a crosslinking agent solution at 30–40°C for 1 h. It was cured at 120–160°C for 2–3 min and then washed and dried. The following indexes were tested:

1. Silk-fibroin adduct (%) = $(W_1 - W_0)/W_0 \times 100$, where W_0 and W_1 are fabric weights before and after coating, respectively.

2. Actual moisture regain was tested according to Chinese National Standard GB9995-88.⁶ Moisture permeability of the coated fabric was tested in line with Chinese National Standard GB/T12704-91.⁷

3. The residual silk-fibroin percentage (RP) after hot-water washing corresponds to the coating fastness to some extent. The coated fabric was immersed in 100 times equivalent distilled water at 80°C for 20 min. The fabric was turned over and pressed once every 5 min. The RP was calculated as follows:

$$R \cdot P = [1 - (W_1 - W_2)/W_1 - W_0] \times 100$$

where W_0 is the fabric weight before coating, W_1 is the fabric weight after coating, and W_2 is the coated fabric weight after hot-water washing.

4. The dyeability of the modified and coated fabric was evaluated by the k/s value after it was dyed with Acid Red G.
6. Surfaces of alkali-amine-hydrolyzed fibers at different treatment times and the surfaces of alkali-amine-hydrolyzed fibers before and after coating were observed with scanning electron microscopy (SEM) with a KYKY-2800 (China Scientific Institute, Beijing, China) at a magnification of 4000.

RESULTS AND DISCUSSION

There are two kinds of modification methods used in the PET finishing: alkaline hydrolysis and aminolysis.⁸

Table I Density and Crystallinity of Fabric (Heat-Set Under Different Temperatures) Before and After Cohydrolysis

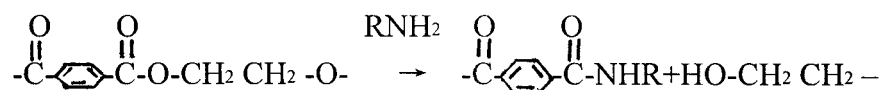
	Heat-Set Temperature (°C)							
	160	165	170	175	180	185	190	200
d_0	1.3749	1.3753	1.3752	1.3758	1.3775	1.3791	1.3792	1.3820
d_1	1.3808	1.3829	1.3827	1.3836	1.3863	1.3897	1.3909	1.3963
Δd	0.0056	0.0076	0.0074	0.0078	0.0088	0.0106	0.0113	0.0143
β_0	0.3525	0.3549	0.3549	0.3598	0.3744	0.3879	0.3886	0.4123
β_1	0.4019	0.4197	0.4184	0.4259	0.4486	0.4775	0.4867	0.5324
$\Delta\beta$	0.0494	0.0648	0.0635	0.661	0.0742	0.0896	0.0981	0.1201

d_0 and β_0 stand for fiber density and crystallinity before hydrolysis, respectively, whereas d_1 and β_1 stand for density and crystallinity after hydrolysis, respectively; $\Delta d = d_1 - d_0$, $\Delta\beta = \beta_1 - \beta_0$. The tension ruler was at 0 cm and the heat-setting time was 0.5 min. R.H. 45%.

Alkaline hydrolysis^{9,10} of PET fiber is a highly developed silk-like modification technique. In theory, PET undergoes a nucleophilic substitution and is hydrolyzed by a NaOH solution. Chain scission occurs and results in considerable WL and hydroxyl and carboxylate end-group formation so as to achieve the silk-like effect. However, alkaline hydrolysis is only a

surface and local reaction resulting in only a small change in the corresponding molecular weight, density, crystallinity, moisture regain, and so on.

Aminolysis^{11,12} of PET is also a nucleophilic reaction. Chain scission also occurs, yielding amide and hydroxyl end groups, which are shown as follows:



where R stands for different alkyl groups. Different amines have different reactivities. Ethylene diamine is used for the purpose of integrating free amine groups onto molecular chains after the reaction. These free amine groups not only provide sites for succeeding reactions (e.g., with epoxides or isocyanate) but also make it possible for acid dye dyeing.

After aminolysis, the molecular weight distribution of the fiber shifts to a lower value, whereas density, crystallinity, and moisture regain have an observable increase, which implies aminolysis is not only a surface reaction. Besides, fiber strength evidently decreases, although WL is comparatively low. Complicated cracks are also observed on the fiber surface, which correspond to the inner tension distribution of the fiber. The aminolysis technique has been used in wool-like finishing.

In comparison, alkaline hydrolysis gives PET a higher WL ratio but cannot provide sufficiently active groups for silk-fibroin fixation and pro-

duces only surface etching pits and craters. Aminolysis has more active amine groups and deeper cracks on PET, but aminolysis has a very slow reaction rate and WL. Neither can meet the requirements of silk-fibroin finishing. Therefore, a novel modification technology was adopted in this research, that is, alkaline-amine cohydrolysis in one bath. It has been proven that a synergistic action does exist to obtain the merits of both WL methods.

Density/Crystallinity Test

It is obvious (see Table I) that after a one-bath NaOH/diamine treatment (cotreatment), considerable increases were observed in the fiber density and crystallinity, which was different from alkaline hydrolysis, whose density and crystallinity were about the same before and after treatment.

It was also observed that the different density and crystallinity increases were obtained at dif-

Table II Effects of Treatment Time of k/s Value for Cohydrolysis Fabric

	Treatment Time (min)							
	10	20	30	40	50	60	70	80
k/s value	0.118	0.143	0.198	0.324	0.640	0.971	1.289	1.846

ferent heat-setting temperatures, indicating that the different heat-treatment conditions affected the inner tension distribution of the fiber and thus the accessibility of the fiber to amine and the modification effects.

It was estimated, because a partial amorphous region was decomposed after the one-bath alkaline/amine treatment and this decomposition tended to happen at the precrystalline area or the edge of the crystalline region, that the density and crystallinity would increase as cotreatment proceeded.

Acid Dye Dyeing

Modified PET can be dyed with an acid dye because of the introduction of amine groups. Even with pure aminolysis, where the WL was only under 5%, an obviously deep red color was observed. However, because aminolysis greatly decreased the fabric strength, further study was not done regarding this aspect.

Table II shows the effects of the cohydrolysis reaction time on the k/s value. As reaction time increased and cohydrolysis progressed, more and more amine groups were produced on the fiber, more dyeing sites were provided for Acid Red G, the color shade deepened, and the k/s value in-

creased. Before 30 min, the increase in k/s was slow and the color was light, implying that very few amine groups were introduced. After 40 min, the k/s value went up markedly, and a turning point appeared at 50 min.

WL

Figure 1 shows the effects of the treatment time on WL from alkaline hydrolysis, aminolysis, and alkali-amine cohydrolysis. All WLs increased with increasing treatment time. WL from aminolysis was by far the lowest. WL from cohydrolysis (covalue) was almost the same as that of alkali hydrolysis initially but later surpassed it rapidly. A comparison of the WL from cohydrolysis with the WL from alkali hydrolysis and aminolysis (addition value) showed a synergistic action that might consist of three stages:

1. In the first stage (reaction time = 0–30 min), it was the attack of NaOH that took the dominant place, and only a little amine took part in the reaction. This was due to the smaller volume and higher reactivity of NaOH, as well as an enormous amorphous region on the fiber surface, so that more NaOH attacked the fiber. However, amin-

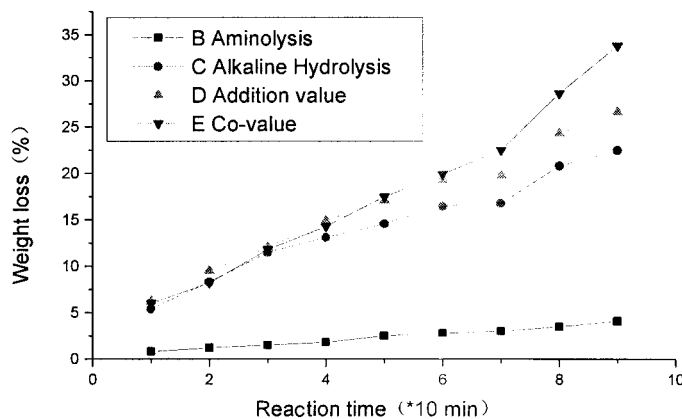


Figure 1 Effects of reaction time on WL for alkali hydrolysis, aminolysis, and cohydrolysis.

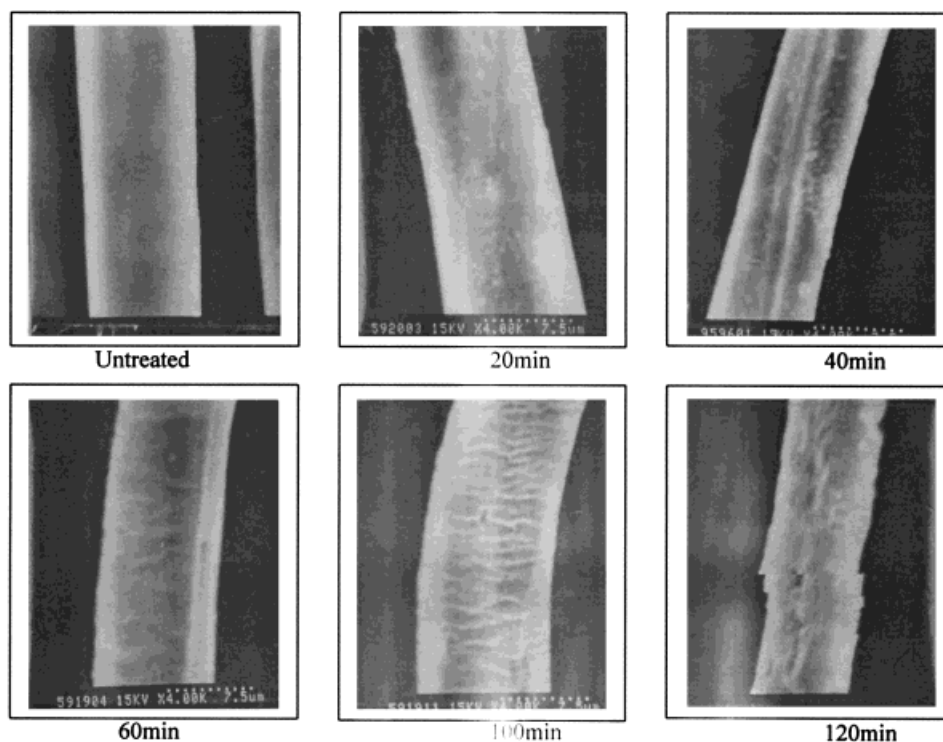


Figure 2 SEM photos of cohydrolyzed fibers at different reaction times.

- olysis was a tension breakage session, which means the amine had a selection for an amorphous region. At this time the fiber was fairly perfect and had few weak points, which prevented the attack of amine. In this stage, the WL of the covalue was almost the same as that of alkali hydrolysis and lower than that of the addition value.
- At the second stage (reaction time = 30–60 min), an outer skin of the fiber had been pilled by alkali (the WL was about 11%), and the area of the amorphous region decreased considerably. In comparison with the first stage, the attack of NaOH slowed down, whereas that of amine acted up, as a result exposing more inner weak points that were sensitive to amine, and formed a certain geometrical reaction band corresponding to the inner tension distribution. It was observed that the covalue of the covalue gradually overtook that of the addition value. This stage also accounted for the turning point of Acid Red G dyeing at 50 min.
 - In the final stage (reaction time > 60 min), more and more amine attacked the fiber along the reaction band. Deeper cracks

were formed. At the same time, NaOH came inside the fiber through these cracks and further decomposed the inner amorphous regions. Eventually, the WL of the covalue increased sharply and was 6.94% higher than that of the addition value at 90 min.

SEM Observation

Figure 2 shows the effects of the different treatment times on the cohydrolysis of the PET surface. Before treatment, the fiber was thick, round, and smooth. As the cohydrolysis started, a few pits appeared on the surface. The pits increased in number, and craters began to appear by 40 min. This indicates the attack mainly of NaOH before 40 min.

Then, shallow transverse cracks occurred on the surface in addition to craters (60 min). At 100 min, many transverse cracks were produced and developed inside the fiber. Bigger craters could also be seen. This stage was mainly the alkali-amine synergistic action.

After 120 min, the fiber was overhydrolyzed. No clear cracks, but instead broader and bigger craters, could be seen. Also, the fiber became much thinner.

Table III Silk-Fibroin Adduct, Real Moisture Regain (MR), and RP of Modified and Unmodified Fabrics with the Same Coating Process

	Fabric		
	Cohydrolysis	Alkali Hydrolysis	Untreated
Silk-fibroin adduct (%)	3.22	2.76	2.82
MR of uncoated fabrics (%)	0.36	0.18	0.15
MR of coated fabrics (%)	0.81	0.44	0.50
Before washing: adduct (%)	3.22	2.76	2.82
After washing	1.98	1.42	1.26
RP of first washing (%)	60.0	53.8	48.1
RP of second washing (%)	57.0	50.0	43.5

Measuring conditions of MR: $T = 21^{\circ}\text{C}$, 47% RH. Silk-fibroin was fixed with glutaraldehyde.

Silk-Fibroin Coating Finishing

After the cohydrolysis, active groups such as amine groups ($-\text{NH}_2$, $-\text{NH}-$), $-\text{OH}$, $-\text{COOH}$, and so on were introduced, and many cracks and craters were also introduced to PET fiber. Moisture regain and the touch of the fabric were improved to some extent, and a more silk-like effect was obtained. However, this improvement was limited, and still more had to be done to really obtain wearing comfort. In this research, the modified PET underwent silk-fibroin finishing that combined real silk fibroin molecules with PET to obtain an advanced silk-like finish.

The silk-fibroin adduct of the cohydrolyzed fabric was obviously higher than those of alkali-hydrolyzed and untreated fabrics (Table III). One reason for this result was that more reactive amino groups were introduced in the cohydrolysis, which took part in the crosslinking reaction and produced chemical combinations between silk fibroin and PET. The other reason was the deeper cracks and bigger craters, which provided stronger mechanical attachment. However, the adducts of alkali-hydrolyzed and untreated PET differed little. This means that alkali hydrolysis did not improve PET's silk-fibroin coating ability.

In addition, the results of moisture regain and RP after hot-water washing also proved that cohydrolysis favors silk-fibroin coating (Table III).

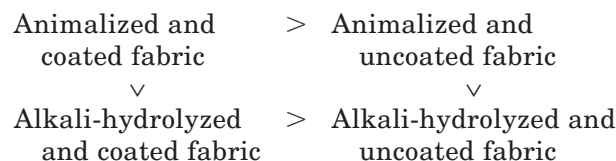
Before coating, the moisture regain of untreated PET was the lowest and that of alkali-hydrolyzed PET increased slightly, whereas cohydrolyzed PET had the highest moisture regain.

After coating, the moisture regain of all samples increased, which indicated that silk fibroin had been introduced on PET. The many hydro-

philic groups of silk fibroin helped to improve the moisture regain. Alkaline-hydrolyzed and untreated samples had similar moisture regains, which were only half of that of the cohydrolyzed sample. Therefore, more silk fibroin was fixed on cohydrolyzed fabric.

RP reflected the fastness of silk-fibroin film to PET to some extent. Table III also shows that the cohydrolyzed sample had the highest RP. Untreated fabric had the lowest RP, whereas the RP value of alkali-hydrolyzed fabric was in between.

PET in itself cannot be dyed with acid dyes. After aminolysis and silk-fibroin coating, more active groups (e.g., $-\text{NH}_2$, $-\text{NH}-$, $-\text{OH}$, $-\text{COOH}$) were introduced, making it acid-dyeable. The sequence of color shades and dyeability of differently treated fabric is



Animalized and coated fabrics had the darkest color and brightest color, which showed more silk-fibroin modification. Alkali-hydrolyzed and coated fabrics had lighter and duller colors, corresponding to less silk-fibroin introduction. Both coated fabrics were more acid-dyeable than uncoated fabrics.

SEM photographs of coated fabrics were also taken (Fig. 3). There were many cracks and craters on the fiber surface before coating, whereas there was obvious attachment after coating, which indicates that a silk-fibroin film was formed.

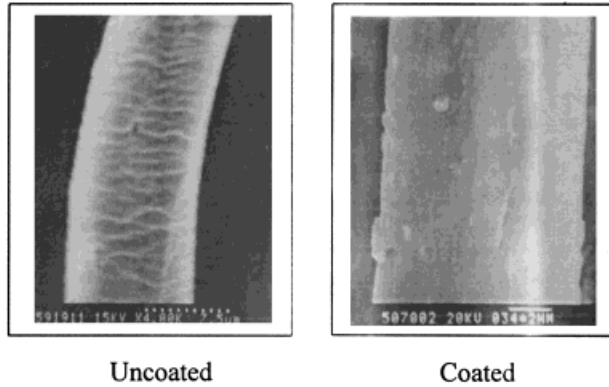


Figure 3 SEM photos of uncoated and coated PET fibers.

CONCLUSIONS

There was a synergistic effect between alkaline hydrolysis and aminolysis of PET microfiber crepe fabric. After the cohydrolysis of alkali-amine treatment, active amino groups and deeper cracks were introduced onto PET fiber. Cohydrolyzed PET had a higher silk-fibroin adduct and better washing retainability (RP), moisture regain, and acid dye dyeability; that is, cohydrolysis

is a promising method for silk-fibroin coating finishing.

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